

## A Machine for Production of Granular Silicon

### Background of the Invention

This invention relates generally to the field of deposition of silicon by chemical vapor deposition, and more particularly to a Machine for Production of Granular Silicon which is of lower cost, more convenient, more reliable, more efficient, provides better quality granules and is better integrated into the overall silicon purification process than existing methods. The use of a pulsing gas flow to circulate granules between a heater and reactor section solves both the granule heating problem and the granule sintering problems that have prevented prior methods from operating for extended time and producing good quality granules. This approach enables use of cheap and reliable resistance heating in contrast to more expensive and less reliable techniques such as microwave and laser heating. Use of an inline non contaminating sieve technique and pulsing gas flow removes silicon product with a more uniform size and returns undersize material which reduces seed generation problems. Online adjustment of the gas pulse shape and flow distribution provides additional control of attrition and seed generation. An optional feedstock recovery system for hydrohalosilane feedstock

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5 allows a more efficient method of recycling the silicon tetrahalide by product,  
allows use of cheaper methods for the production of the hydrohalosilane and  
provides flexibility in balancing the overall product slate of a silicon purification  
facility.

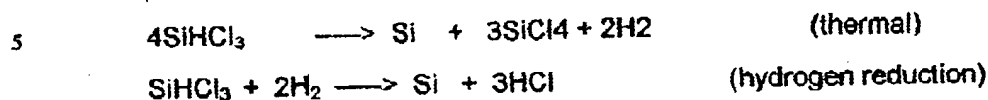
10 This invention relates generally to the field of silicon purification, and more  
particularly to a machine for production of high purity silicon granules by the  
decomposition of a high purity silicon containing gas, such as silane,  
trichlorosilane or tribromosilane, which can be designed to optimize the overall  
efficiency of such a silicon purification process.

15 The production of high purity electronic grade silicon is the critical first step  
of the entire multi-billion dollar semi-conductor industry. The basic process, used  
by most manufacturers consists of three steps; conversion of metallurgical grade  
silicon into a hydrohalosilane such as trichlorosilane, purification of this material  
20 by distillation and other means, and decomposition of the material back to silicon.  
The Ethyl process, directly reduces silicon tetrafluoride to silane with a byproduct  
of aluminum trifluoride.

The decomposition reactors are all rod reactors except for fluid bed  
reactors operated on silane as part of the Ethyl Process. Fluid bed reactors have  
25 significant capital, operating and energy advantages but have proved difficult to  
implement. The only operating fluid bed units produce a dusty product  
contaminated with hydrogen that is not widely accepted.

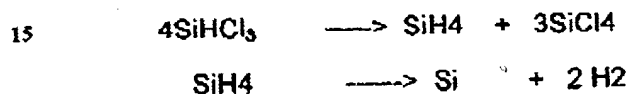
There are two decomposition reactions for hydrohalosilanes; thermal  
decomposition and hydrogen reduction. (Trichlorosilane is used in the examples  
30 but bromine or iodine can be substituted for chlorine, fluorine cannot)

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All halosilane reactors incorporate both and consequently produce an effluent, which has a range of silicon hydrohalides and tetrahalides and hydrogen halides and hydrogen.

10            The essence of the process is impure silicon in, pure silicon out plus small impurity streams. To accomplish this there are large recycle streams of hydrogen, silicon and halide containing streams and is important not to produce low value by-products or waste streams. Union Carbide developed an approach of producing silane by disproportionation then decomposing the silane



It can be seen that the overall reaction is the same as the thermal decomposition reaction.

20            The major use for the polycrystalline silicon is in production of single crystal silicon via melting and growth of single crystal silicon boules in Czochralski crystal pullers. Such pullers have specific requirements with regard to feeding the granules (also known as beads), contamination, and ease of melting etc. which must be met in order to use silicon beads. Kajimoto et al documents some

25            of these issues in US Patent No. 5,037,503.

The purity requirements for electronic grade silicon are severe with specifications for hydrogen at about 30-50ppma, parts per million atomic, oxygen at 0.5-1.5 ppma and carbon at 0.1-0.25 ppma with specifications for donors such as boron,

30            phosphorus and aluminum in the ppba, parts per billion atomic, and metals in the U.S. Patent Application of S. M. Lord – Page 5

5 ppta, parts per trillion atomic. Thus all materials which come in contact with the silicon must be virtually free of metals and donors and have very small amounts of oxygen, hydrogen and carbon which are transferable to the silicon. Historically such specifications have progressively tightened and this trend can be expected to continue. Other trends in the industry are to larger and larger wafer diameters  
10 with the current transition from 200 mm to 300 mm wafers being underway. This trend has led to the need to pull larger and larger diameter crystals which in turn leads to the desire to add silicon to the crystal growing furnace while the crystal is being pulled. This can be done conveniently with silicon granules which melt easily and are very pure and hence there is a need for such high purity granules.  
15 A further historical trend is the decreasing availability of cheap hydro-electric power which has been the prime source of energy for the very inefficient rod reactors which leads to the increasing need to improve energy efficiency in the deposition process.

Because of the lower energy, capital cost and operating cost of fluid bed reactors  
20 much work has been done to develop this technology but the problem of meeting the above ever tighter purity specifications is more acute with the use of fluid bed reactors because they are more susceptible to materials problems as the silicon product is in physical contact with the wall, which thus must be at or close to the deposition temperature. This requires hot walls in contrast to the rod reactors,  
25 which typically have cooled walls. Furthermore fluid bed reactors do not have the internal heat generation provided by the electrical heating of the rod in rod reactors and so must add heat in some other way. If this heat is added through the walls, the walls must be hotter than the silicon product. A further problem is that the materials coming into the reactor can only be preheated to a temperature  
30 below their thermal decomposition temperature which is 350-450°C for most

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5 feedstock materials. For high throughput fluid bed reactors putting in the additional heat to bring the temperature up to the desired decomposition temperature of greater than 800°C is very difficult. The major operational problem is sintering of the beads in the reactor and the resultant plugging of the reactor, the major purity problems are metals, carbon, oxygen and hydrogen in  
10 the bulk and surface of the product and the major problem in feeding beads to the crystal puller is difficulty in controlling the bead flow due to variation in shape and size.

The sintering appears to be more prevalent as the temperature, deposition rate, silicon containing gas concentration and bead size increases and less prevalent  
15 as the fluidizing gas flow rate increases. Hence a violently fluidized bed will have a lower tendency to sinter but may tend to blow over more dust and will require more heat.

It has been accepted that it is important to have a reactor that does not contaminate the product and that the use of metal reactors is not feasible, see  
20 Ling U.S. Pat. No 3,012,861 and Ingle U.S. Pat. No. 4,416,913 and hence metal contamination can be resolved by not contacting the beads with any metal parts. Similarly contact with carbon or carbon containing materials leads to carbon contamination so graphite or silicon carbide parts are usually coated with silicon, carbon can also come in through contaminants in the inlet gases such as carbon  
25 monoxide, carbon dioxide and methane. Oxygen normally comes in through oxygen containing compounds such as water, carbon monoxide and carbon dioxide in the inlet gases and hence all carbon and oxygen containing compounds are removed from the gas streams to as great a degree as is practicable. Oxygen containing materials such as silicon oxide (quartz) are

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5 frequently used as containment materials, see Ingle above, and can be used in  
 contact with silicon although care must be taken to prevent erosion.  
 Hydrogen contamination is primarily caused during the deposition process when  
 hydrogen remains trapped in the bead. This is a time, temperature and  
 deposition rate dependent process which has been described by A. M. Beers et  
 10 al "CVD Silicon Structures Formed by Amorphous and Crystalline Growth,"  
 Journal of Crystal Growth, 64, (1983) 563-571. For rapid deposition rates of the  
 order of 2-3 micron/minute, which are desired in commercial reactors, the silicon  
 surface temperature must exceed 800°C. Typical rod reactors usually operate  
 above this temperature as do halosilane based fluid bed reactors and thus such  
 15 reactors do not suffer from this problem. The current silane based commercial  
 fluid bed reactors operate below this temperature in at least part of the reactor  
 and consequently have dusting problems see Gautreaux and Allen US Patent #  
 4,784,840 and require a second dehydrogenation step as described by Allen in  
 US Patent # 5,242,671.  
 20 The problem of size and shape is not as important but most polycrystalline  
 consumers would prefer large round beads because they flow better and have  
 less surface area, thus less risk of contamination. Large beads require more gas  
 flow to fluidize and hence more heat to bring said gas up to operating  
 temperature.  
 25 US Patent 4,092,446 by Padovani describes an optimized system using a fluid  
 bed and extensive recycle of materials. US Patents 5,798,137 and 5,810,934 by  
 Lord describe a fluid bed capable of operating with or without recycle on a variety  
 of feedstock. Various fluid bed patents describe methods of operating and of  
 30 heating. US Patent 5,374,413 by Kim et al. describe use of two feed streams  
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5 one of which is used to prevent wall deposition, which would block the passage  
of the microwaves used for heating the beads. There has been much effort to  
use silane in a fluid bed because it was more concentrated and gave more silicon  
per mole of feedstock, unfortunately it has proved too prone to sintering at high  
concentrations and thus all silane fluid bed reactors operate at high dilution rates  
10 which negates the benefit of the concentration. Thus a process penalty is paid in  
producing the silane and an additional penalty is paid in providing high purity  
diluent.

All these systems take the effluent from the decomposition reactor as it is  
15 cooled down and removed from the reactor and then separate and recycle the  
components. Thus significant effort goes into the recycle process but most prior  
reactor designs ignore the issue with the exception of Padovani in US Patent  
4,207,360 where he selects a high temperature, 1100°C, to convert the silicon  
tetrachloride to silicon and thus uses a graphite brick lining coated with silicon  
20 carbide. Unfortunately this material contaminated the silicon produced with  
carbon and thus the process failed commercially as the silicon could not be sold.  
The above patents by Lord neglect the system integration issue except to  
suggest that the halogen used to etch the reactor be one that matches the  
halogens used in the process and Kim also neglects the system integration  
25 issue. Instead both point out that the use of silicon oxide is preferred because of  
its purity and cost and expend a great deal of effort on providing the heat to the  
reactor in a way which will reduce wall deposits. Kim suggests using microwaves  
and Lord suggests use of laser and/or chlorine heating in conjunction with  
microwaves. Heating the reactor up to the even higher temperatures needed to  
30 convert silicon tetrahalides make this problem even worse and the attempt is not  
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5 made. Operating on silane at lower temperatures (600-700°C) as is done in US Patent 4,784,840 requires low deposition rates and results in dusty product contaminated with hydrogen thus requiring post treatment as described in US Patent 5,242,671.

Other attempts to provide reactor heat include Van Slooten in US Patent  
10 4,992,245 who describes an annular heated fluidized bed operating on silane where the beads enter the heating zone annulus at the top and exit at the bottom back to the reactor and Iya in US patent 4,818,495 who describes a reactor with an upper heating zone and a lower reacting zone with a cooled gas distribution zone.

15 Other aspects of reactor design that have received attention are the related problems of managing the size distribution of granules in the reactor, providing new seed particles and selectively removing large particles. Ingle U.S. Pat. No. 4,416,913 described a circulating bed that would selectively remove larger  
20 particles and Iya (U.S. pat No. 4,424,199) described a boot device for the same purpose. Padovani described using two temperature zones to increase the natural attrition of the granules at lower temperature. Lord described in more detail a method for segregation using a tapered bed and how the attrition was related to the kinetic power of the incoming jet. Iya in US patent 4,424,199  
25 describes a fluid jet seed particle generator inserted in a "hydrogen boot" located below the reactor, which was intended to separate the small seed particles from the product.

Recovery of heat from the effluent has not received much attention but Lord described a method for recovering heat from the outgoing beads by a heat  
30 exchanger, which heated up the incoming silane.

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5 The primary overall system deficiency in the prior technology is that it neglects the opportunities in the temperature regime between the deposition temperature, which is typically between 750°C and 1150°C, and the condensation temperature of the halosilanes in the effluent, which are typically below room temperature. The effluent gases are allowed to cool slowly and continue to react through this large temperature range thus producing more of the undesired silicon tetrahalide and condensation and polymerization of silicon dichloride  $\text{SiCl}_2$  monomer on the walls of the effluent piping to form explosive solids such as  $\text{Si}_2\text{Cl}_6$ ,  $\text{Si}_3\text{Cl}_8$  and  $\text{Si}_4\text{Cl}_{10}$  with no effort made to adjust the equilibrium conditions or to quench the reaction.

15 In this range the species in the effluent change composition with temperature and there is always an optimum temperature for recovery of the desired components, which is typically 800-1000°C. At this temperature the desired hydrohalosilanes such as trichlorosilane and dichlorosilane are at or near a maximum and thus can be recovered which has great impact on the overall silicon and chlorine balance. Addition of the undesirable silicon tetrahalide and hydrogen pushes the equilibrium in the direction of the desired hydrohalosilanes but the reactors must operate hotter and with greater hydrogen recycle to convert the undesired silicon tetrachloride. This in turn results in lower silicon production, more difficult materials problems, greater energy requirements, more production of  $\text{SiCl}_2$  and  $\text{SiCl}_3$  monomer and consequent formation of explosive solids.

25 One approach to resolving the said problem of explosive solids is the injection of chlorine or hydrogen chloride in the effluent piping as suggested by Lord. This technique resolves this problem but generates silicon tetrachloride, which is not a desirable product. Another approach is to operate at lower temperature e.g. 800-900°C where the formation of  $\text{SiCl}_2$  and  $\text{SiCl}_3$  monomer is reduced but this lowers

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5 silicon production and prevents recycle of silicon tetrachloride in the reactor. This neglect of the overall system optimization issue in the reactor design means that even reactors that are functionally capable of making granular silicon will not necessarily reap the full benefits anticipated. This particularly in the case where it is desired to replace trichlorosilane based rod reactors, which consume silicon  
10 tetrachloride with fluid bed reactors, which do not. This will mean a whole redesign of the facility to accommodate the recycle of the silicon tetrachloride and to generate additional trichlorosilane, which will seriously impact the economics.

15 A major deficiency of the prior technology in the design of the reactors themselves is in resolving the multiple issues, which surround the supply of heat to fluidized beds for use as silicon deposition reactors. One standard way to heat a fluidized bed is through the walls because the heat transfer from the wall to the particles is very good and wall heaters can be easily and cheaply built using  
20 electric heating coils. Another standard way is to preheat the gas reactants. A further standard approach is to recover heat from both the solid and gaseous effluent of the reactor by means of heat exchange. A yet further standard approach is to recycle unused reactant and or carrier gas. In a silicon deposition reactor there are problems facing all of these approaches. If the wall is heated  
25 then it is by definition hotter than the bed particles and hence more likely to be deposited on as the reaction rate is strongly influenced by temperature. Hence a hot wall causes wall deposits which are a loss of product, increase the resistance to heat transfer through the wall and can cause breakage of the reactor on cool-down due to differential thermal expansion. There is also the  
30 problem that the heat load is localized to the inlet area where the incoming gases

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5 are heated up to reaction temperature. Thus hot beads may be present in the reactor but unable to circulate down to the inlet zone fast enough to provide sufficient heat.

10 Heating the gas reactants is restricted by the thermal decomposition of the silicon bearing gases at around 350-400°C. Thus the gases cannot be heated above this temperature without depositing in the heater or in the inlet to the reactor. This problem is further compounded by heat conducted back into the inlet from hot beads located just above the inlet of the silicon bearing gases. The surface temperature of these beads should be over 800°C to prevent hydrogen  
15 contamination, hence there is a high temperature gradient between the beads at 800°C and the inlet which needs to be below the thermal decomposition temperature of the silicon containing gases which is 350°C. Recovery of heat is difficult because of the tendency of the silicon containing gas to form wall deposits which in turn means the wall temperature must be below 350°C which is  
20 difficult when cooling gases or solids which are at 800°C or greater. Recycle of unused reactants or carrier gas is also difficult for the same decomposition reason. The recycle gas must be cooled to below the thermal decomposition temperature of the silicon containing gases before mixing with them.

25 Thus the prior technology has attempted to deal with the heating issue in a variety of ways. Ingle, U.S. Pat. No. 4,416,913, noted the use of microwaves to heat the silicon beads directly through the quartz wall which itself is not heated by microwaves. Poong et al. in U.S. Pat. No. 4,900,411 advises using  
30 microwaves and notes the need to cool the wall and the distributor grid in order to prevent silicon deposits, which can then absorb the microwaves. Iya in U.S.

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5 Pat. No. 4,818,495 also suggests cooling the distributor grid and providing a heating zone above the reacting zone to compensate. Kim et al in U.S. Pat. No. 5,374,413 notes that cooling of the wall is not effective in preventing wall deposits and greatly increases power consumption and suggests a partition between the reacting and heating zone. Ingle see above and Van Slooten in U.S. Pat. No. 4,992,245. Neither Iya in US Patent # 4,818,495 nor Van Slooten in US Patent # 4,992,245 provided means for the heated beads to travel down to the reacting area in sufficient quantity to heat the incoming gases and offset the distributor cooling. Lord in U.S. Pat. No. 5,798,137 suggests use of "jet heating" where lasers are used to heat through the inlet jet itself or chlorine is added to react with silane in the jet region. Lord in US Patent 5,810,934, also suggests using an isolation tube between the inner tube containing the silicon containing gases and the outer tube containing the hot beads in order to control the wall temperature of the inner tube below the decomposition temperature. This suffers from the two disadvantages of reducing the heat transfer and the heat transfer rate. Hence only a portion of the available heat can be recovered thus requiring additional bead cooling and the surface area must be larger than would be required other wise. Lord in fact recognizes this and provides an alternate approach using a water-cooled bead cooler.

25 All the prior technology makes provision for dilution of the silicon bearing gas before the mixture is fed to the reactor stream and so the inlet gas temperature is still limited by the decomposition temperature of the silicon bearing gas, which is typically around 350°C. Kim and Van Slooten also make provision for a separate entry for a carrier gas into the heating zone, which is separated from the reaction zone by a partition, and they claim this gas may be heated up to the reaction

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5 temperature although in their examples the actual temperature is below that. In  
 Van Slooten's example the inlet gas is 500°C compared to reactor temperatures  
 of 650°C at the top and 550°C and a heating zone temperature of 660°C. In  
 Kim's examples the carrier gas preheat temperature was 250°C and 35°C. The  
 prior technology had difficulty in reaching the required high temperatures, greater  
 10 than 800°C, without contaminating the product or plugging the reactor. These  
 high temperatures are needed, particularly at the gas inlet, for production of  
 hydrogen and dust free product. A critical deficiency of the prior technology, with  
 the exception of Lord in US Patents # 5,798,137 and 5,810,934, is the failure to  
 recognize the importance of the need to maintain high temperatures according to  
 15 the experimental data and theoretical relationships in the article of A. M. Beers et  
 al "CVD Silicon Structures Formed by Amorphous and Crystalline Growth,"  
 Journal of Crystal Growth, 64. (1983) 563-571. This article details the  
 relationship of temperature, time and deposition rate with higher deposition rates  
 requiring higher temperatures and times in order to crystallize the deposited  
 20 amorphous silicon and release the codeposited hydrogen.

In the prior technology the inlet area has the most serious problems in product  
 quality because of a combination of factors all of which tend to prevent the  
 needed crystallization to produce polycrystalline silicon and remove hydrogen  
 25 and/or other codeposited elements such as halogens. This area has the highest  
 silicon bearing gas concentrations, the lowest temperatures and the least post  
 deposit time for the beads. The deposit rates tend to be highest at the inlet  
 because of the high silicon containing gas concentrations and the rapid  
 decomposition of the silicon bearing gases once the temperature is above 500°C.  
 30 The temperatures are lower because the incoming gases are cold and cool the  
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5 beads near the inlet as the gases warm up. Finally the beads are removed at or near the bottom of the reactor which is also the inlet for the gases thus the beads removed have just been deposited on and hence have little time to crystallize the recent deposits and dehydrogenate. Of these factors the most important one is the temperature because the crystallization rate is strongly dependent on  
10 temperature. Frequently the prior technology aggravates this problem by cooling the distributor grid. Thus in the prior technology most of the reaction and deposition occurs near the inlet and much of this deposit is unsuitable because of its powdery nature and high hydrogen content. Iya in U.S. Pat. No. 4,818,495 shows a temperature profile where the zone just above the grid is at 500°C and  
15 the top of the bed is at 770°C. Hence the product would be very dusty and contaminated with hydrogen.

Similarly in Van Slooten U.S. Patent No. 4,992,245 the distributor surface is cooled to a temperature between 200-400°C and he states in his example that  
20 the temperature at the top of the fluidized bed is 923 K (700°C) and at the bottom is 823 K ( 600°C). Again the product would be dusty and contaminated with hydrogen. Kim has the reactive gas distributor cooled to 318°C in his example 2 and has a CVD reaction temperature of 930°C. Since the partition isolates the reaction zone from the heating zone and is half the bed height the beads next to  
25 the reactive gas inlet are much colder than the upper part of the reactor as the hot beads from the heater section do not mix with them. These beads are primarily heated through the quartz partition which itself is deposited on by the silicon containing gases in the reaction zone. This silicon wall deposit will be hotter than the beads in the reaction zone and will thus grow at a more rapid rate.  
30 The reactor described in the Van Slooten U.S. Patent No. 4,992,245 also faces

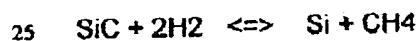
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5 this problem of wall deposit on the partition. It is apparent that the provision of a partition does not avoid the problem of wall deposits it merely relocates them to the partition. Thus the requirement for a partition is an additional deficiency in the prior technology. The provision of a partition can help the bead quality if the beads are removed from the heating zone of the partitioned reactor since the  
10 beads have more time at a higher temperature without any deposition. Unfortunately such post deposition crystallization and dehydrogenation suffers from the problem that the hydrogen must diffuse out through the complete deposit thickness and this can take several hours or days as shown by Allen in US Patent # 5,242,671. This amount of time is usually not available as a practical  
15 matter since it requires a significantly larger reactor and also higher temperatures (1000-1100°C).

Lord In U.S. Pat. No. 5,798,137 recognizes the need to remove hydrogen as the deposition occurs in order to minimize the distance the hydrogen has to diffuse  
20 out and provides localized "jet heating" at the inlet with lasers and or chlorine. The major deficiencies of this approach are that laser heating is expensive and inefficient and the equipment is high maintenance and chlorine heating is expensive, reduces yield and contributes contaminants. A further deficiency is that success in raising the inlet zone temperature means more heat is conducted  
25 back to the inlet, which is not cooled, and thus causes wall deposits within the inlet.

The provision of a partition requires a carrier gas to fluidize the beads on the heating side of the partition. Since this is not a reactive gas it can be heated  
30 above the decomposition temperature of the silicon bearing gas and both Kim U.S. Patent Application of S. M. Lord – Page 17

5 and Van Slooten claim this feature in their patents. However the sensible heat of the carrier gas is not used to directly heat the reacting beads and neither Van Slooten nor Kim claim the possibility of heating the carrier gas above the reaction temperature. In the example by Kim the carrier gas is 4.0 mole/min of hydrogen at 250°C and the reactive gas is 3.1 mole/min of trichlorosilane and 6.0 mol/min of hydrogen at 100°C. Neither temperature is above the decomposition temperature of TCS (350°C) or remotely close to the stated CVD reaction temperature of 930°C. In fact more hydrogen is used as a diluent in the reactive gas than is used as "heated" carrier gas. The CVD reaction temperature of 930°C is low for trichlorosilane deposition by the hydrogen reduction reaction and will result in lower yield of silicon as is shown in example 1 where the TCS feed is 0.35 mol/min and the silicon deposition rate is 1104 grams over ten hours which calculates to 1.85 grams/min or .066 mol/min. This is a yield of 18.8% of the silicon in the TCS. The preferred temperature for hydrogen reduction is above 1000°C and preferably 1100-1250°C as noted in Padovani U.S. Patent No. 4,207,360. Obtaining such temperatures required use of high temperature materials such as silicon carbide coated graphite walls, which could operate significantly hotter than the beads. Unfortunately this approach causes carbon contamination of the silicon making it unusable. The source of the contamination is primarily a reversible gas phase reaction;



Silicon Carbide + Hydrogen  $\rightleftharpoons$  Silicon + Methane

The methane gas is formed at the silicon carbide walls and mixes in with the silicon beads where it decomposes to form silicon carbide thus contaminating the beads. At such high temperatures the silicon carbide diffuses rapidly through the silicon wall deposit to continually replenish the surface.

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Thus the approaches taken by the prior technology to heat the reactor suffer from an inability to obtain the desired high temperatures in the inlet region and/or required for high silicon yield without forming severe reactor or partition wall deposits, plugging the inlet or distribution means, resorting to expensive, exotic and unreliable heating means or contaminating the product. A further deficiency of most of the prior technology is its failure to provide sufficient post deposition time at temperature to complete the crystallization and dehydrogenation of the product needed to produce low dust and hydrogen content silicon beads.

15 A further major deficiency in the prior technology has been the problem of sintering of the granules into large lumps which can occur on the flow distributor or grid, on the wall or in the bulk of the bed. The sintering appears to be more prevalent as the temperature, deposition rate, silicon containing gas concentration and bead size increases and less prevalent as the fluidizing gas flow rate increases. Hence a violently fluidized bed will have a lower tendency to sinter but may tend to blow over more dust and will require more heat. Efforts to control the problem at the distributor have included cooling it as described by Iya, in U.S. Pat. No. 4,684,513, and Poong, in U.S. Pat. No. 4,900,411. Such efforts have led to large thermal inefficiencies and to problems with dust formation and hydrogen contamination. Lord in the above patents claims that avoiding internals of any kind eliminates the problem of plugging the internals and suggests a single jet. The prior technology did not recognize the inherent contradiction in the technology; it is desired to grow particles without them sticking together. The majority of the growth mechanism is the sticking of small micro-particles to the large granules of the bed and the granules must be sticky in order for the micro

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5 particles to attach. Lord describes at length the mechanisms involved and discusses the Tamman temperature limit below which the particles are not sticky yet fails to consider the inherent contradiction of assuming the micro particles will stick to the granules but the granules will not stick to each other even when covered with sticky micro particles. Thus the cooling of the grid can be seen to  
10 be effective because the particles are no longer sticky and inherently the granules will be dusty as the dust has not adhered. The observation that high velocities and low feedstock concentrations improves the situation indicates that there is the possibility of operation in a regime where the granules are sticky but can be unstuck from each other when sufficient energy is provided and there is  
15 not a huge excess of sticky microparticles. The prior technology did not address this issue but relied on the use of the experimentally observed benefit of high velocities and low silicon containing gas concentrations which compounded the heating and contamination problems of the prior reactors and increased their size and cost because the reactors are larger and there is more external equipment  
20 for recycle of the diluent gases.

A yet further deficiency linked to the stickiness of the particles is the failure of the prior technology to effectively segregate out the larger granules for removal as product. Ingle in US Pat. No. 4,416,913 and Iya in U.S. Pat. No. 4,424,199  
25 describe attempts to segregate the particles in a dilute phase and Lord in U.S. Pat. No. 5,798,137 describes segregation in a dense phase using a tapered reactor. All were moderately successful in dry runs without silicon containing gases but not successful with operation with silicon containing gases, because when the silicon containing gases are present the beads are stickier and more  
30 violent bed action is required which tends to mix the bed rather than segregating.

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5 it. This deficiency is also related to the requirement for seed particle generation  
 since removal of only large granules means far fewer particles are removed and  
 hence far fewer seed particles need to be generated. This deficiency is  
 particularly aggravated when the seed particles are generated at the same  
 location that the product is removed, as is the case for both Iya and Lord above  
 10 since the newly generated seeds are also removed.

Another deficiency of the prior technology is in the appearance of the granules.  
 The granules produced by the prior technology tend to be dusty, dull and  
 misshapen compared to the customers preference for dust free, shiny and round  
 15 granules. Gautreaux in U.S. Pat. No. 4, 784,840 recognized the need for less  
 dusty granules and provides a reactor with two modes of operation, high  
 deposition and high dust followed by low deposition and low dust to seal in the  
 dust from the previous operation. This is still carried out at low temperature 620-  
 650°C and merely reduces the dust. Lord in U.S. Pat. No. 5,798,137 describes  
 20 the mechanism which tends to cause the formation of round beads and its  
 dependence on Reynolds number, unfortunately the required conditions are very  
 difficult to meet for a silane based reactor unless 100% silane is used and the  
 beads are very large. Lord also describes a laser surface annealing techniques  
 which flash melts the surface to provide a shiny finish. The problem with such a  
 25 technique is applying it evenly to all the surface of a large number of particles  
 and the cost and difficulty of operation of the laser based system.

While the prior technology has usually recognized one or more of the problems  
 involved in the design of fluid beds for silicon deposition none of the prior  
 30 technology has been able to resolve the design problems without compromising  
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5 one or more aspects and as a consequence the only commercially functioning  
fluid bed system, which is designed according to the patents of Allen and  
Gautreaux, produces a very dusty product that requires additional treatment  
steps before it can meet specifications and has only a limited market because of  
the problems of using a dusty material. Other designs have failed to produce a  
10 material that meets specifications or have been unable to operate because of  
sintering or plugging. Finally designs that may be capable of producing  
specification product and operating successfully tend to use expensive heating  
methods such as lasers or microwaves and in the cases of trichlorosilane based  
reactors may not be usable without extensive redesign and construction of the  
15 trichlorosilane production facilities. In contrast the proposed technology has  
resolved the design problems without compromising any major aspects, without  
using expensive heating techniques or excessive external facilities for recycle  
and can be used in an existing trichlorosilane facility with only minor changes  
when used with the optional feedstock recovery system.

20

### Summary of the Invention

The primary object of the invention is to provide a design for a fluidized  
25 bed reactor which make high purity silicon granules in a single reactor which will  
be safe and easy to operate and commercially viable with a variety of feedstocks  
and optimized for the overall system efficiency.

Another object of the invention is to make low cost granules.

Another object of the invention is to use a low cost reactor.

30 A further object of the invention is to have low operating costs.

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5 Yet another object of the invention is to make very large granules.  
Still yet another object of the invention is to make round granules.  
Another object of the invention is to make shiny granules.  
Another object of the invention is to be able to scale up easily.  
Still yet another object of the invention is to minimize external support  
10 equipment.

Another object of the invention is to maximize silicon yield from feedstock.

Other objects and advantages of the present invention will become  
apparent from the following descriptions, taken in connection with the  
15 accompanying drawings, wherein, by way of illustration and example, an  
embodiment of the present invention is disclosed.

A Machine for Production of Granular Silicon comprising separate injection  
of silicon containing gases and non silicon containing gases, heating the non  
20 silicon containing gases above the reaction temperature, cooling each injection  
location of the silicon containing gases, and provision of one or more stages with  
each stage having a heating section located below a reacting section and a  
mechanism that pulses granules back and forth between the heating and  
reacting sections.

25 Where there are multiple stages each reactor section has one or more injection  
nozzles for gases which promote additional reaction, in the silane reactor the gas  
to the reaction section would be silane, for the hydrohalosilane, e.g.  
trichlorosilane or tribromosilane, reactor the gas to the reactor section could be

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- 5 the hydrohalosilane alone, ultra high purity hydrogen alone or a combination of the two.

Heat is recovered from the granules by direct contact with a high purity non silicon depositing or reacting gases: such gases can be hydrogen, helium,  
 10 argon, nitrogen, silicon tetrachloride and silicon tetrabromide and must be low in carbon and oxygen containing contaminants, such as oxygen, water, carbon monoxide, carbon dioxide and methane, which contaminants must be below 1 ppmv, parts per million by volume, and preferably below 10ppbv, parts per billion by volume. Gases such as silicon trichlorosilane and silane are not usable  
 15 because they decompose, hydrogen chloride, hydrogen bromide or mixtures of gases, which react such as a silicon tetrachloride, and hydrogen mixture are not usable because they can react with the granules.

The heat exchanger in which the silicon containing gases are heated avoids  
 20 overheating the wall by using hot liquid or condensing vapor maintained within a temperature range which cannot cause decomposition of the gases, which temperature range is typically between 200-400°C but more particularly between 300-350°C.

25 The sieving device by which silicon granules are sieved uses one or more sieves manufactured from non contaminating sieve material and the undersized granules are returned to the reactor and the noncontaminating sieve material is selected from materials which contain silicon such as single crystal silicon, polycrystalline silicon, silicon oxide, silicon nitride, silicon oxynitride and silicon  
 30 carbide and where the abradable surfaces are low in contaminants such as

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- 5 boron, phosphorus, aluminum, arsenic, iron, copper and other metals, such  
contaminants will typically be below 1000 ppmwt and preferably below 100  
ppmwt

When used with a hydrohalosilane feedstock such as trichlorosilane it is  
10 preferred to use the optional feedstock recovery section, where a silicon  
quadrahalide such as silicon tetrachloride or silicon tetrabromide is injected,  
mixed with the reactor effluent then quenched at an optimal temperature (850-  
950°C) to recover the silicon hydrohalides such as trichlorosilane and  
dichlorosilane.

- 15 Joints between external equipment and the reactor, which transmit hot gases or  
solids, are cooled using one or more microchannels positioned and localized to  
cool the elastomeric O-ring to a temperature such that decomposition of the O-  
ring or increased permeability of the o-ring to oxygen, water and carbon dioxide  
20 does not cause significant contamination or excessive heat loss, such  
temperature is typically 25-300°C and preferably 50-150°C for o-rings made from  
high purity fluorocarbon o-rings such as Viton, Kalrez and Teflon.

External flow control of each injection point is preferred and such flow control  
25 may be direct with flow control of each nozzle done independently, indirect by  
means of a flow distribution device such as a manifold or a combination of the  
two where some nozzles are ganged in groups.

The shape of the pulse and/or the distribution of flow between nozzles may be  
30 adjusted to control the generation of new particles without changing the total

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- 5 flow. It is preferred that the flow of gas to each nozzle is controlled before the heater/s and an even more preferred option is where multiple separate flows are heated in the same heater.

- 10 In a preferred combination for the use of silane as a feedstock there are two or more stages, high purity hydrogen is used for the non silicon containing gas to the first heating section, for the cooling of the granular silicon and for return of undersize granules to the reactor, the sieving device is made from polycrystalline silicon, the feedstock recovery system is not used, cooled joints are used for all the inlets and outlets of the reactor, the silane heat exchanger uses a condensing
- 15 vapor maintained in the temperature range 340-360°C and each gas injection location is independently controlled.

- In a preferred combination of the above claims for the use of trichlorosilane and/or dichlorosilane as a feedstock, where there are, two or more stages, high
- 20 purity hydrogen is used for the non silicon containing gas to the first heating section and to the second reacting section, for the cooling of the granular silicon and for return of undersize granules to the reactor, the sieving device is made from polycrystalline silicon, the feedstock recovery system is used and silicon tetrachloride is injected to cool the effluent from 1100°C to 900°C and recover
- 25 hydrohalosilanes for recycle, cooled joints are used for all the inlets and outlets of the reactor, the chlorosilane heat exchanger uses a condensing vapor maintained in the temperature range 340-360°C and each gas injection location is independently controlled.

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5 In a preferred variation the heater section is of smaller diameter than the reactor section above it and connected by a tapered section, angle of said tapered section to be between 10 and 80 degrees from the vertical and preferably between 30-60 degrees from the vertical.

10 The heaters used in the heating sections may be resistance heaters, inductive RF heaters, microwave heaters, lamp heaters or lasers but are preferably resistance heaters.

A high efficiency cyclone is used to remove dust from the effluent gases

15

A silicon etching gas or mixture of gases may be injected through one or more nozzles for the purpose of etching wall deposits from all or part of the reactor, such gases may be elemental halides such as chlorine or bromine, hydrogen halides such as hydrogen chloride or hydrogen bromide or combinations of  
20 hydrogen and silicon tetrahalides such as silicon tetrachloride or silicon tetrabromide.

The reactor is supported upon a weigh cell, capable of weighing the reactor and contents and measuring the intermittent force exerted by the pulsing gas and the  
25 connections to and from the reactor are flexible enough to allow the slight deflection required by the weigh cell, said deflection to be less than 1mm and preferably less than 0.5mm, and the thermal expansion of the reactor relative to the support structure, said thermal expansion to be less than 1" (25mm) and preferably less than 1/4" (6mm).

30

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5 A variation on the design is where all or a portion of the non silicon containing  
gases are heated to a temperature below the reaction temperature outside the  
heating section then heated to a temperature above the reactor temperature  
inside the heater prior to entry to the reactor section.

In a yet further variation the second stage heater section does contain some  
10 residual silicon dust or silicon containing gases from the first stage reactor  
section that can form a wall deposit.

The drawings constitute a part of this specification and include exemplary  
15 embodiments to the invention, which may be embodied in various forms. It is to  
be understood that in some instances various aspects of the invention may be  
shown exaggerated or enlarged to facilitate an understanding of the invention.

20

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5

A Machine for Production of Granular Silicon

*Marked up Version.*

10

U.S. Patent Application of:

15

Stephen Michael Lord

20

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5 Related Applications

Application Number 09/507,154

Filing Date 02/18/2000

GRP Art Unit 1754

Inventor: Stephen M. Lord

10 Title: Method for Improving the Efficiency of A Silicon Purification Process

Application Number 09/589563

Filing Date 06/06/00

GRP Art Unit 1754

Inventor: Stephen M. Lord

15 Title: Methods for Heating a Fluidized Bed Silicon Deposition Apparatus

5

## A Machine for Production of Granular Silicon

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10

### Background of the Invention

15

This invention relates generally to the field of deposition of silicon by chemical vapor deposition, and more particularly to a Machine for Production of Granular Silicon which is of lower cost, more convenient, more reliable, more efficient, provides better quality granules and is better integrated into the overall silicon purification process than existing methods. The use of a pulsing gas flow to circulate granules between a heater and reactor section solves both the granule heating problem and the granule sintering problems that have prevented prior methods from operating for extended time and producing good quality granules. This approach enables use of cheap and reliable resistance heating in contrast to more expensive and less reliable techniques such as microwave and laser heating. Use of an inline non contaminating sieve technique and pulsing gas flow removes silicon product with a more uniform size and returns undersize material which reduces seed generation problems. Online adjustment of the gas pulse shape and flow distribution provides additional control of attrition and seed generation. An optional feedstock recovery system for hydrohalosilane feedstock

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5 allows a more efficient method of recycling the silicon tetrahalide by product,  
allows use of cheaper methods for the production of the hydrohalosilane and  
provides flexibility in balancing the overall product slate of a silicon purification  
facility.

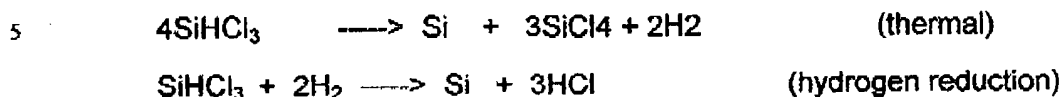
10 This invention relates generally to the field of silicon purification, and more  
particularly to a machine for production of high purity silicon granules by the  
decomposition of a high purity silicon containing gas, such as silane,  
trichlorosilane or tribromosilane, which can be designed to optimize the overall  
efficiency of such a silicon purification process

15 The production of high purity electronic grade silicon is the critical first step  
of the entire multi-billion dollar semi-conductor industry. The basic process, used  
by most manufacturers consists of three steps; conversion of metallurgical grade  
silicon into a hydrohalosilane such as trichlorosilane, purification of this material  
20 by distillation and other means, and decomposition of the material back to silicon.  
The Ethyl process, directly reduces silicon tetrafluoride to silane with a  
byproduct of aluminum trifluoride.

The decomposition reactors are all rod reactors except for fluid bed  
reactors operated on silane as part of the Ethyl Process. Fluid bed reactors have  
25 significant capital, operating and energy advantages but have proved difficult to  
implement. The only operating fluid bed units produce a dusty product  
contaminated with hydrogen that is not widely accepted.

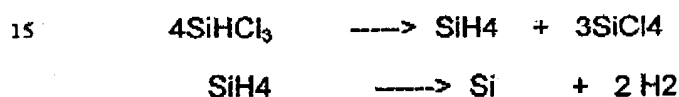
There are two decomposition reactions for hydrohalosilanes; thermal  
decomposition and hydrogen reduction. (Trichlorosilane is used in the examples  
30 but bromine or iodine can be substituted for chlorine, fluorine cannot)

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All halosilane reactors incorporate both and consequently produce an effluent, which has a range of silicon hydrohalides and tetrahalides and hydrogen halides and hydrogen.

10 The essence of the process is impure silicon in, pure silicon out plus small impurity streams. To accomplish this there are large recycle streams of hydrogen, silicon and halide containing streams and is important not to produce low value by-products or waste streams. Union Carbide developed an approach of producing silane by disproportionation then decomposing the silane



It can be seen that the overall reaction is the same as the thermal decomposition reaction.

20 The major use for the polycrystalline silicon is in production of single crystal silicon via melting and growth of single crystal silicon boules in Czochralski crystal pullers. Such pullers have specific requirements with regard to feeding the granules (also known as beads), contamination, ease of melting etc. which must be met in order to use silicon beads. Kajimoto et al documents some of  
25 these issues in US Patent No. 5,037,503.

The purity requirements for electronic grade silicon are severe with specifications for hydrogen at about 30-50ppma(parts per million atomic), oxygen at 0.5-1.5 ppma and carbon at 0.1-0.25 ppma with specifications for donors such  
30 as boron, phosphorus and aluminum in the ppba, (parts per billion atomic), and  
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5 metals in the ppta, (parts per trillion atomic). Thus all materials which come in  
 contact with the silicon must be virtually free of metals and donors and have very  
 small amounts of oxygen, hydrogen and carbon which are transferable to the  
 silicon. Historically such specifications have progressively tightened and this  
 trend can be expected to continue. Other trends in the industry are to larger and  
 10 larger wafer diameters with the current transition from 200 mm to 300 mm wafers  
 being underway. This trend has led to the need to pull larger and larger diameter  
 crystals which in turn leads to the desire to add silicon to the crystal growing  
 furnace while the crystal is being pulled. This can be done conveniently with  
 silicon granules which melt easily and are very pure and hence there is a need  
 15 for such high purity granules.

A further historical trend is the decreasing availability of cheap hydro-electric  
 power which has been the prime source of energy for the very inefficient rod  
 reactors which leads to the increasing need to improve energy efficiency in the  
 deposition process.

20 Because of the lower energy, capital cost and operating cost of fluid bed reactors  
 much work has been done to develop this technology but the problem of meeting  
 the above ever tighter purity specifications is more acute with the use of fluid bed  
 reactors because they are more susceptible to materials problems as the silicon  
 product is in physical contact with the wall, which thus must be at or close to the  
 25 deposition temperature. This requires hot walls in contrast to the rod reactors,  
 which typically have cooled walls. Furthermore fluid bed reactors do not have  
 the internal heat generation provided by the electrical heating of the rod in rod  
 reactors and so must add heat in some other way. If this heat is added through  
 the walls, the walls must be hotter than the silicon product. A further problem is  
 30 that the materials coming into the reactor can only be preheated to a temperature

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5 below their thermal decomposition temperature which is 350-450°C for most  
feedstock materials. For high throughput fluid bed reactors putting in the  
additional heat to bring the temperature up to the desired decomposition  
temperature of greater than 800°C is very difficult. The major operational  
problem is sintering of the beads in the reactor and the resultant plugging of the  
10 reactor, the major purity problems are metals, carbon, oxygen and hydrogen in  
the bulk and surface of the product and the major problem in feeding beads to  
the crystal puller is difficulty in controlling the bead flow due to variation in shape  
and size.

The sintering appears to be more prevalent as the temperature, deposition rate,  
15 silicon containing gas concentration and bead size increases and less prevalent  
as the fluidizing gas flow rate increases. Hence a violently fluidized bed will have  
a lower tendency to sinter but may tend to blow over more dust and will require  
more heat.

It has been accepted that it is important to have a reactor that does not  
20 contaminate the product and that the use of metal reactors is not feasible, see  
Ling U.S. Pat. No 3,012,861 and Ingle U.S. Pat. No. 4,416,913 and hence metal  
contamination can be resolved by not contacting the beads with any metal parts.  
Similarly contact with carbon or carbon containing materials leads to carbon  
contamination so graphite or silicon carbide parts are usually coated with silicon,  
25 carbon can also come in through contaminants in the inlet gases such as carbon  
monoxide, carbon dioxide and methane. Oxygen normally comes in through  
oxygen containing compounds such as water, carbon monoxide and carbon  
dioxide in the inlet gases and hence all carbon and oxygen containing  
compounds are removed from the gas streams to as great a degree as is  
30 practicable. Oxygen containing materials such as silicon oxide (quartz) are  
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5 frequently used as containment materials, see Ingle above, and can be used in contact with silicon although care must be taken to prevent erosion.

Hydrogen contamination is primarily caused during the deposition process when hydrogen remains trapped in the bead. This is a time, temperature and deposition rate dependent process which has been described by A. M. Beers et al "CVD Silicon Structures Formed by Amorphous and Crystalline Growth,"  
10 Journal of Crystal Growth, 64. (1983) 563-571. For rapid deposition rates of the order of 2-3 micron/minute which are desired in commercial reactors the silicon surface temperature must exceed 800°C. Typical rod reactors usually operate above this temperature as do halosilane based fluid bed reactors and thus such  
15 reactors do not suffer from this problem. The current silane based commercial fluid bed reactors operate below this temperature in at least part of the reactor and consequently have dusting problems see Gautreaux and Allen US Patent # 4,784,840 and require a second dehydrogenation step as described by Allen in US Patent # 5,242,671.

20 The problem of size and shape is not as important but most polycrystalline consumers would prefer large round beads because they flow better and have less surface area, thus less risk of contamination. Large beads require more gas flow to fluidize and hence more heat to bring said gas up to operating temperature.

25 US Patent 4,092,446 by Padovani describes an optimized system using a fluid bed and extensive recycle of materials. US Patents 5,798,137 and 5,810,934 by Lord describe a fluid bed capable of operating with or without recycle on a variety of feedstock. Various fluid bed patents describe methods of operating and of  
30 heating. US Patent 5,374,413 by Kim et al. describe use of two feed streams  
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5 one of which is used to prevent wall deposition which would block the passage of  
the microwaves used for heating the beads. There has been much effort to use  
silane in a fluid bed because it was more concentrated and gave more silicon per  
mole of feedstock, unfortunately it has proved too prone to sintering at high  
concentrations and thus all silane fluid bed reactors operate at high dilution rates  
10 which negates the benefit of the concentration. Thus a process penalty is paid in  
producing the silane and an additional penalty is paid in providing high purity  
diluent.

All these systems take the effluent from the decomposition reactor as it is  
15 cooled down and removed from the reactor and then separate and recycle the  
components. and significant effort goes into the recycle process but most prior  
reactor designs ignore the issue with the exception of Padovani in US Patent  
4,207,360 where he selects a high temperature, 1100°C, to convert the silicon  
tetrachloride to silicon and thus uses a graphite brick lining coated with silicon  
20 carbide. Unfortunately this material contaminated the silicon produced with  
carbon and thus the process failed commercially as the silicon could not be sold.  
The above patents by Lord neglect the system integration issue except to  
suggest that the halogen used to etch the reactor be one that matches the  
halogens used in the process and Kim also neglects the system integration  
25 issue. Instead both point out that the use of silicon oxide is preferred because of  
its purity and cost and expend a great deal of effort on providing the heat to the  
reactor in a way which will reduce wall deposits. Kim suggest using microwaves  
and Lord suggests use of laser and/or chlorine heating in conjunction with  
microwaves. Heating the reactor up to the even higher temperatures needed to  
30 convert silicon tetrahalides make this problem even worse and the attempt is not  
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5 made. Operating on silane at lower temperatures (600-700°C) as is done in US Patent 4,784,840 requires low deposition rates and results in dusty product contaminated with hydrogen thus requiring post treatment as described in US Patent 5,242,671.

Other attempts to provide reactor heat include Van Slooten in US Patent  
10 4,992,245 who describes an annular heated fluidized bed operating on silane where the beads enter the heating zone annulus at the top and exit at the bottom back to the reactor and Iya in US patent 4,818,495 who describes a reactor with an upper heating zone and a lower reacting zone with a cooled gas distribution zone.

15 Other aspects of reactor design that has received attention are the related problems of managing the size distribution of granules in the reactor, providing new seed particles and selectively removing large particles. Ingle U.S. Pat. No. 4,416,913 described a circulating bed that would selectively remove larger  
20 particles and Iya (U.S. pat No. 4,424,199) described a boot device for the same purpose. Padovani described using two temperature zones to increase the natural attrition of the granules at lower temperature. Lord described in more detail a method for segregation using a tapered bed and how the attrition was related to the kinetic power of the incoming jet. Iya in US patent 4,424,199  
25 describes a fluid jet seed particle generator inserted in a "hydrogen boot" located below the reactor, which was intended to separate the small seed particles from the product.

Recovery of heat from the effluent has not received much attention but Lord described a method for recovering heat from the outgoing beads by a heat  
30 exchanger, which heated up the incoming silane.

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5 The primary overall system deficiency in the prior technology is that it neglects the opportunities in the temperature regime between the deposition temperature, which is typically between 750°C and 1150°C, and the condensation temperature of the halosilanes in the effluent, which are typically below room temperature. The effluent gases are allowed to cool slowly and continue to react through this  
10 large temperature range thus producing more of the undesired silicon tetrahalide and condensation and polymerization of silicon dichloride  $\text{SiCl}_2$  monomer on the walls of the effluent piping to form explosive solids such as  $\text{Si}_2\text{Cl}_6$ ,  $\text{Si}_3\text{Cl}_8$  and  $\text{Si}_4\text{Cl}_{10}$  with no effort made to adjust the equilibrium conditions or to quench the reaction.

15 In this range the species in the effluent change composition with temperature and there is always an optimum temperature for recovery of the desired components, which is typically 800-1000°C. At this temperature the desired hydrohalosilanes such as trichlorosilane and dichlorosilane are at or near a maximum and thus can be recovered which has great impact on the overall  
20 silicon and chlorine balance. Addition of the undesirable silicon tetrahalide and hydrogen pushes the equilibrium in the direction of the desired hydrohalosilanes but the reactors must operate hotter and with greater hydrogen recycle to convert the undesired silicon tetrachloride. This in turn results in lower silicon production, more difficult materials problems, greater energy requirements, more  
25 production of  $\text{SiCl}_2$  and  $\text{SiCl}_3$  monomer and consequent formation of explosive solids.

One approach to resolving the said problem of explosive solids is the injection of chlorine or hydrogen chloride in the effluent piping as suggested by Lord. This technique resolves this problem but generates silicon tetrachloride which is not a  
30 desirable product. Another approach is to operate at lower temperature e.g. 800-

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5 900°C where the formation of  $\text{SiCl}_2$  and  $\text{SiCl}_3$  monomer is reduced but this lowers  
silicon production and prevents recycle of silicon tetrachloride in the reactor. This  
neglect of the overall system optimization issue in the reactor design means that  
even reactors that are functionally capable of making granular silicon will not  
necessarily reap the full benefits anticipated. This particularly in the case where it  
10 is desired to replace trichlorosilane based rod reactors, which consume silicon  
tetrachloride with fluid bed reactors, which do not. This will mean a whole  
redesign of the facility to accommodate the recycle of the silicon tetrachloride  
and to generate additional trichlorosilane, which will seriously impact the  
economics.

15

A major deficiency of the prior technology in the design of the reactors  
themselves is in resolving the multiple issues, which surround the supply of heat  
to fluidized beds for use as silicon deposition reactors. One standard way to heat  
a fluidized bed is through the walls because the heat transfer from the wall to the  
20 particles is very good and wall heaters can be easily and cheaply built using  
electric heating coils. Another standard way is to preheat the gas reactants. A  
further standard approach is to recover heat from both the solid and gaseous  
effluent of the reactor by means of heat exchange. A yet further standard  
approach is to recycle unused reactant and or carrier gas. In a silicon deposition  
25 reactor there are problems facing all of these approaches. If the wall is heated  
then it is by definition hotter than the bed particles and hence more likely to be  
deposited on as the reaction rate is strongly influenced by temperature. Hence  
a hot wall causes wall deposits which are a loss of product, increase the  
resistance to heat transfer through the wall and can cause breakage of the  
30 reactor on cool-down due to differential thermal expansion. There is also the  
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5 problem that the heat load is localized to the inlet area where the incoming gases are heated up to reaction temperature. Thus hot beads may be present in the reactor but unable to circulate down to the inlet zone fast enough to provide sufficient heat.

10 Heating the gas reactants is restricted by the thermal decomposition of the silicon bearing gases at around 350-400°C. Thus the gases cannot be heated above this temperature without depositing in the heater or in the inlet to the reactor. This problem is further compounded by heat conducted back into the inlet from hot beads located just above the inlet of the silicon bearing gases. The  
 15 surface temperature of these beads should be over 800°C to prevent hydrogen contamination, hence there is a high temperature gradient between the beads at 800°C and the inlet which needs to be below the thermal decomposition temperature of the silicon containing gases which is 350°C. Recovery of heat is difficult because of the tendency of the silicon containing gas to form wall  
 20 deposits which in turn means the wall temperature must be below 350°C which is difficult when cooling gases or solids which are at 800°C or greater. Recycle of unused reactants or carrier gas is also difficult for the same decomposition reason. The recycle gas must be cooled to below the thermal decomposition temperature of the silicon containing gases before mixing with them.

25

Thus the prior technology has attempted to deal with the heating issue in a variety of ways. Ingle, U.S. Pat. No. 4,416,913 noted the use of microwaves to heat the silicon beads directly through the quartz wall which itself is not heated by microwaves. Poong et al. in U.S. Pat. No. 4,900,411 advises using  
 30 microwaves and notes the need to cool the wall and the distributor grid in order  
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5 to prevent silicon deposits, which can then absorb the microwaves. Iya in U.S. Pat. No. 4,818,495 also suggests cooling the distributor grid and providing a heating zone above the reacting zone to compensate. Kim et al in U.S. Pat. No. 5,374,413 notes that cooling of the wall is not effective in preventing wall deposits and greatly increases power consumption and suggests a partition  
10 between the reacting and heating zone. Ingle see above and Van Slooten in U.S. Pat. No. 4,992,245. Neither Iya in US Patent # 4,818,495 nor Van Slooten in US Patent # 4,992,245 provided means for the heated beads to travel down to the reacting area in sufficient quantity to heat the incoming gases and offset the distributor cooling. Lord in U.S. Pat. No.  
15 5,798,137 suggests use of "jet heating" where lasers are used to heat through the inlet jet itself or chlorine is added to react with silane in the jet region. Lord in US Patent 5,810,934, also suggests using an isolation tube between the inner tube containing the silicon containing gases and the outer tube containing the hot beads in order to control the wall temperature of the inner tube below the  
20 decomposition temperature. This suffers from the two disadvantages of reducing the heat transfer and the heat transfer rate. Hence only a portion of the available heat can be recovered thus requiring additional bead cooling and the surface area must be larger than would be required other wise. Lord in fact recognizes this and provides an alternate approach using a water-cooled bead cooler.

25

All the prior technology makes provision for dilution of the silicon bearing gas before the mixture is fed to the reactor stream and so the inlet gas temperature is still limited by the decomposition temperature of the silicon bearing gas which is typically around 350°C. Kim and Van Slooten also make provision for a separate  
30 entry for a carrier gas into the heating zone, which is separated from the reaction U.S. Patent Application of S. M. Lord – Page 14



5 zone by a partition, and they claim this gas may be heated up to the reaction  
temperature although in their examples the actual temperature is below that. In  
Van Slooten's example the inlet gas is 500°C compared to reactor temperatures  
of 650°C at the top and 550°C and a heating zone temperature of 660°C. In  
Kim's examples the carrier gas preheat temperature was 250°C and 35°C. The  
10 prior technology had difficulty in reaching the required high temperatures, greater  
than 800°C, without contaminating the product or plugging the reactor. These  
high temperatures are needed, particularly at the gas inlet, for production of  
hydrogen and dust free product. A critical deficiency of the prior technology, with  
the exception of Lord in US Patents # 5,798,137 and 5,810,934, is the failure to  
15 recognize the importance of the need to maintain high temperatures according to  
the experimental data and theoretical relationships in the article of A. M. Beers et  
al "CVD Silicon Structures Formed by Amorphous and Crystalline Growth,"  
Journal of Crystal Growth, 64. (1983) 563-571. This article details the  
relationship of temperature, time and deposition rate with higher deposition rates  
20 requiring higher temperatures and times in order to crystallize the deposited  
amorphous silicon and release the codeposited hydrogen.

In the prior technology the inlet area has the most serious problems in product  
quality because of a combination of factors all of which tend to prevent the  
25 needed crystallization to produce polycrystalline silicon and remove hydrogen  
and/or other codeposited elements such as halogens. This area has the highest  
silicon bearing gas concentrations, the lowest temperatures and the least post  
deposit time for the beads. The deposit rates tend to be highest at the inlet  
because of the high silicon containing gas concentrations and the rapid  
30 decomposition of the silicon bearing gases once the temperature is above 500°C.

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5 The temperatures are lower because the incoming gases are cold and cool the beads near the inlet as the gases warm up. Finally the beads are removed at or near the bottom of the reactor which is also the inlet for the gases thus the beads removed have just been deposited on and hence have little time to crystallize the recent deposits and dehydrogenate. Of these factors the most important one is

10 the temperature because the crystallization rate is strongly dependent on temperature. Frequently the prior technology aggravates this problem by cooling the distributor grid. Thus in the prior technology most of the reaction and deposition occurs near the inlet and much of this deposit is unsuitable because of its powdery nature and high hydrogen content. Iya in U.S. Pat. No. 4,818,495

15 shows a temperature profile where the zone just above the grid is at 500°C and the top of the bed is at 770°C. Hence the product would be very dusty and contaminated with hydrogen.

Similarly in Van Slooten U.S. Patent No. 4,992,245 the distributor surface is

20 cooled to a temperature between 200-400°C and he states in his example that the temperature at the top of the fluidized bed is 923 K (700°C) and at the bottom is 823 K ( 600°C). Again the product would be dusty and contaminated with hydrogen. Kim has the reactive gas distributor cooled to 318°C in his example 2 and has a CVD reaction temperature of 930°C. Since the partition isolates the

25 reaction zone from the heating zone and is half the bed height the beads next to the reactive gas inlet are much colder than the upper part of the reactor as the hot beads from the heater section do not mix with them. These beads are primarily heated through the quartz partition which itself is deposited on by the silicon containing gases in the reaction zone. This silicon wall deposit will be

30 hotter than the beads in the reaction zone and will thus grow at a more rapid rate.

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5 The reactor described in the Van Slooten U.S. Patent No. 4,992,245 also faces this problem of wall deposit on the partition. It is apparent that the provision of a partition does not avoid the problem of wall deposits it merely relocates them to the partition. Thus the requirement for a partition is an additional deficiency in the prior technology. The provision of a partition can help the bead quality if the  
10 beads are removed from the heating zone of the partitioned reactor since the beads have more time at a higher temperature without any deposition.

Unfortunately such post deposition crystallization and dehydrogenation suffers from the problem that the hydrogen must diffuse out through the complete deposit thickness and this can take several hours or days as shown by Allen in  
15 US Patent # 5,242,671. This amount of time is usually not available as a practical matter since it requires a significantly larger reactor and also higher temperatures (1000-1100°C).

Lord in U.S. Pat. No. 5,798,137 recognizes the need to remove hydrogen as the  
20 deposition occurs in order to minimize the distance the hydrogen has to diffuse out and provides localized "jet heating" at the inlet with lasers and or chlorine. The major deficiencies of this approach are that laser heating is expensive and inefficient and the equipment is high maintenance and chlorine heating is expensive, reduces yield and contributes contaminants. A further deficiency is  
25 that success in raising the inlet zone temperature means more heat is conducted back to the inlet, which is not cooled, and thus causes wall deposits within the inlet.

The provision of a partition requires a carrier gas to fluidize the beads on the  
30 heating side of the partition. Since this is not a reactive gas it can be heated

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5 above the decomposition temperature of the silicon bearing gas and both Kim  
and Van Slooten claim this feature in their patents. However the sensible heat of  
the carrier gas is not used to directly heat the reacting beads and neither Van  
Slooten nor Kim claim the possibility of heating the carrier gas above the reaction  
temperature. In the example by Kim the carrier gas is 4.0 mole/min of hydrogen  
10 at 250°C and the reactive gas is 3.1 mole/min of trichlorosilane and 6.0 mol/min  
of hydrogen at 100°C. Neither temperature is above the decomposition  
temperature of TCS (350°C) or remotely close to the stated CVD reaction  
temperature of 930°C. In fact more hydrogen is used as a diluent in the reactive  
gas than is used as "heated" carrier gas. The CVD reaction temperature of  
15 930°C is low for trichlorosilane deposition by the hydrogen reduction reaction and  
will result in lower yield of silicon as is shown in example 1 where the TCS feed is  
0.35 mol/min and the silicon deposition rate is 1104 grams over ten hours which  
calculates to 1.85 grams/min or .066 mol/min. This is a yield of 18.8% of the  
silicon in the TCS. The preferred temperature for hydrogen reduction is above  
20 1000°C and preferably 1100-1250°C as noted in Padovani U.S. Patent No.  
4,207,360. Obtaining such temperatures required use of high temperature  
materials such as silicon carbide coated graphite walls, which could operate  
significantly hotter than the beads. Unfortunately this approach causes carbon  
contamination of the silicon making it unusable. The source of the contamination  
25 is primarily a reversible gas phase reaction;



Silicon Carbide + Hydrogen  $\rightleftharpoons$  Silicon + Methane

The methane gas is formed at the silicon carbide walls and mixes in with the  
silicon beads where it decomposes to form silicon carbide thus contaminating the

5 beads. At such high temperatures the silicon carbide diffuses rapidly through the silicon wall deposit to continually replenish the surface.

Thus the approaches taken by the prior technology to heat the reactor suffer from an inability to obtain the desired high temperatures in the inlet region and/or  
 10 required for high silicon yield without forming severe reactor or partition wall deposits, plugging the inlet or distribution means, resorting to expensive, exotic and unreliable heating means or contaminating the product. A further deficiency of most of the prior technology is its failure to provide sufficient post deposition time at temperature to complete the crystallization and dehydrogenation of the  
 15 product needed to produce low dust and hydrogen content silicon beads.

A further major deficiency in the prior technology has been the problem of sintering of the granules into large lumps which can occur on the flow distributor or grid, on the wall or in the bulk of the bed. The sintering appears to be more  
 20 prevalent as the temperature, deposition rate, silicon containing gas concentration and bead size increases and less prevalent as the fluidizing gas flow rate increases. Hence a violently fluidized bed will have a lower tendency to sinter but may tend to blow over more dust and will require more heat. Efforts to control the problem at the distributor have included cooling it as described by Iya  
 25 in U.S. Pat. No. 4,684,513 and Poong in U.S. Pat. No. 4,900,411. Such efforts have led to large thermal inefficiencies and to problems with dust formation and hydrogen contamination. Lord in the above patents claims that avoiding internals of any kind eliminates the problem of plugging the internals and suggests a single jet. Unfortunately ~~a single jet tends to form a channel through the bed and~~  
 30 ~~thus the sintering occurs around the jet with the result the bed itself plugs.~~ The U.S. Patent Application of S. M. Lord – Page 19

5 prior technology did not recognize the inherent contradiction in the technology; it is desired to grow particles without them sticking together. The majority of the growth mechanism is the sticking of small micro- particles to the large granules of the bed and the granules must be sticky in order for the micro particles to attach. Lord describes at length the mechanisms involved and discusses the Tamman  
10 temperature limit below which the particles are not sticky yet fails to consider the inherent contradiction of assuming the micro particles will stick to the granules but the granules will not stick to each other even when covered with sticky micro particles. Thus the cooling of the grid can be seen to be effective because the particles are no longer sticky and inherently the granules will be dusty as the dust  
15 has not adhered. The observation that high velocities and low feedstock concentrations improves the situation indicates that there is the possibility of operation in a regime where the granules are sticky but can be unstuck from each other when sufficient energy is provided and there is not a huge excess of sticky microparticles. The prior technology did not address this issue but relied  
20 on the use of the experimentally observed benefit of high velocities and low silicon containing gas concentrations which compounded the heating and contamination problems of the prior reactors and increased their size and cost because the reactors are larger and there is more external equipment for recycle of the diluent gases.

25

A yet further deficiency linked to the stickiness of the particles is the failure of the prior technology to effectively segregate out the larger granules for removal as product. Ingle in US Pat. No. 4,416,913 and Iya in U.S. Pat. No. 4,424,199 describe attempts to segregate the particles in a dilute phase and Lord in U.S.  
30 Pat. No. 5,798,137 describes segregation in a dense phase using a tapered U.S. Patent Application of S. M. Lord – Page 20

5 reactor. Both All were moderately successful in dry runs without silicon  
containing gases but not successful with operation with silicon containing gases,  
because when the silicon containing gases are present the beads are stickier  
and more violent bed action is required which tends to mix the bed rather than  
segregating it. This deficiency is also related to the requirement for seed particle  
10 generation since removal of only large granules means far fewer particles are  
removed and hence far fewer seed particles need to be generated. This  
deficiency is particularly aggravated when the seed particles are generated at the  
same location that the product is removed as is the case for both Iya and Lord  
above since the newly generated seeds are also removed.

15

Another deficiency of the prior technology is in the appearance of the granules.  
The granules produced by the prior technology tend to be dusty, dull and  
misshapen compared to the customers preference for dust free, shiny and round  
granules. Gautreaux in U.S. Pat. No.4, 784,840 recognized the need for less  
20 dusty granules and provides a reactor with two modes of operation, high  
deposition and high dust followed by low deposition and low dust to seal in the  
dust from the previous operation. This is still carried out at low temperature 620-  
650°C and merely reduces the dust. Lord in U.S. Pat. No. 5,798,137 describes  
the mechanism which tends to cause the formation of round beads and its  
25 dependence on Reynolds number, unfortunately the required conditions are very  
difficult to meet for a silane based reactor unless 100% silane is used and the  
beads are very large. Lord also describes a laser surface annealing techniques  
which flash melts the surface to provide a shiny finish. The problem with such a  
technique is applying it evenly to all the surface of a large number of particles  
30 and the cost and difficulty of operation of the laser based system.

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5

While the prior technology has usually recognized one or more of the problems involved in the design of fluid beds for silicon deposition none of the prior technology has been able to resolve the design problems without compromising one or more aspects and as a consequence the only commercially functioning fluid bed system, which is designed according to the patents of Allen and Gautreaux, produces a very dusty product that requires additional treatment steps before it can meet specifications and has only a limited market because of the problems of using a dusty material. Other designs have failed to produce a material that meets specifications or have been unable to operate because of sintering or plugging. Finally designs that may be capable of producing specification product and operating successfully tend to use expensive heating methods such as lasers or microwaves and in the cases of trichlorosilane based reactors may not be usable without extensive redesign and construction of the trichlorosilane production facilities. In contrast the proposed technology has resolved the design problems without compromising any major aspects, without using expensive heating techniques or excessive external facilities for recycle and can be used in an existing trichlorosilane facility with only minor changes when used with the optional feedstock recovery system.

25

### Summary of the Invention

The primary object of the invention is to provide a design for a fluidized bed reactor which make high purity silicon granules in a single reactor which will

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5 be safe and easy to operate and commercially viable with a variety of feedstocks  
and optimized for the overall system efficiency.

Another object of the invention is to make low cost granules.

Another object of the invention is to use a low cost reactor.

A further object of the invention is to have low operating costs.

10 Yet another object of the invention is to make very large granules.

Still yet another object of the invention is to make round granules.

Another object of the invention is to make shiny granules.

Another object of the invention is to be able to scale up easily.

15 Still yet another object of the invention is to minimize external support  
equipment.

Another object of the invention is to maximize silicon yield from feedstock.

Other objects and advantages of the present invention will become  
apparent from the following descriptions, taken in connection with the  
20 accompanying drawings, wherein, by way of illustration and example, an  
embodiment of the present invention is disclosed.

A Machine for Production of Granular Silicon comprising separate injection  
of silicon containing gases and non silicon containing gases, heating the non  
25 silicon containing gases above the reaction temperature, cooling each injection  
location of the silicon containing gases, and provision of one or more stages with  
each stage having a heating section located below a reacting section and a  
mechanism that pulses granules back and forth between the heating and  
reacting sections.

30

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5 Where there are multiple stages each reactor section has one or more injection  
nozzles for gases which promote additional reaction, in the silane reactor the gas  
to the reaction section would be silane, for the hydrohalosilane, e.g.  
trichlorosilane or tribromosilane, reactor the gas to the reactor section could be  
the hydrohalosilane alone, ultra high purity hydrogen alone or a combination of  
10 the two.

Heat is recovered from the granules by direct contact with a high purity non  
silicon depositing or reacting gases: such gases can be hydrogen, helium,  
argon, nitrogen, silicon tetrachloride and silicon tetrabromide and must be low in  
15 carbon and oxygen containing contaminants, such as oxygen, water, carbon  
monoxide, carbon dioxide and methane, which contaminants must be below 1  
ppmv, parts per million by volume, wt and preferably below 10ppbv, parts per  
billion by volumewt. Gases such as silicon trichlorosilane and silane are not  
usable because they decompose, hydrogen chloride, hydrogen bromide or  
20 mixtures of gases, which react such as a silicon tetrachloride, and hydrogen  
mixture are not usable because they can react with the granules.

The heat exchanger in which the silicon containing gases are heated avoids  
overheating the wall by using hot liquid or condensing vapor maintained within a  
25 temperature range which cannot cause decomposition of the gases, which  
temperature range is typically between 200-400°C but more particularly between  
300-350°C.

The sieving device by which silicon granules are sieved uses one or more sieves  
30 manufactured from non contaminating sieve material and the undersized

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- 5 granules are returned to the reactor and the noncontaminating sieve material is selected from materials which contain silicon such as single crystal silicon, polycrystalline silicon, silicon oxide, silicon nitride, silicon oxynitride and silicon carbide and where the abratable surfaces are low in contaminants such as boron, phosphorus, aluminum, arsenic, iron, copper and other metals, such  
10 contaminants will typically be below 1000 ppmwt and preferably below 100 ppmwt

When used with a hydrohalosilane feedstock such as trichlorosilane it is preferred to use the optional feedstock recovery section, where a silicon  
15 quadrahalide such as silicon tetrachloride or silicon tetrabromide is injected, mixed with the reactor effluent then quenched at an optimal temperature (850-950°C) to recover the silicon hydrohalides such as trichlorosilane and dichlorosilane.

- 20 Joints between external equipment and the reactor, which transmit hot gases or solids, are cooled using one or more microchannels positioned and localized to cool the elastomeric O-ring to a temperature such that decomposition of the O-ring or increased permeability of the o-ring to oxygen ,water and carbon dioxide does not cause significant contamination or excessive heat loss , such  
25 temperature is typically 25-300°C and preferably 50-150°C for o-rings made from high purity fluorocarbon o-rings such as Viton, Kalrez and Teflon.

External flow control of each injection point is preferred and such flow control may be direct with flow control of each nozzle done independently, indirect by

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5 means of a flow distribution device such as a manifold or a combination of the two where some nozzles are ganged in groups.

The shape of the pulse and/or the distribution of flow between nozzles may be adjusted to control the generation of new particles without changing the total  
10 flow. It is preferred that the flow of gas to each nozzle is controlled before the heater/s and an even more preferred option is where multiple separate flows are heated in the same heater.

In a preferred combination for the use of silane as a feedstock there are two or  
15 more stages, high purity hydrogen is used for the non silicon containing gas to the first heating section, for the cooling of the granular silicon and for return of undersize granules to the reactor, the sieving device is made from polycrystalline silicon, the feedstock recovery system is not used, cooled joints are used for all the inlets and outlets of the reactor, the silane heat exchanger uses a condensing  
20 vapor maintained in the temperature range 340-360°C and each gas injection location is independently controlled.

In a preferred combination of the above claims for the use of trichlorosilane and/or dichlorosilane as a feedstock, where there are, two or more stages, high  
25 purity hydrogen is used for the non silicon containing gas to the first heating section and to the second reacting section, for the cooling of the granular silicon and for return of undersize granules to the reactor, the sieving device is made from polycrystalline silicon, the feedstock recovery system is used and silicon tetrachloride is injected to cool the effluent from 1100°C to 900°C and recover  
30 hydrohalosilanes for recycle , cooled joints are used for all the inlets and outlets

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5 of the reactor, the chlorosilane heat exchanger uses a condensing vapor maintained in the temperature range 340-360°C and each gas injection location is independently controlled.

10 In a preferred variation the heater section is of smaller diameter than the reactor section above it and connected by a tapered section, angle of said tapered section to be between 10 and 80 degrees from the vertical and preferably between 30-60 degrees from the vertical.

15 The heaters used in the heating sections may be resistance heaters, inductive RF heaters, microwave heaters, lamp heaters or lasers but are preferably resistance heaters.

A high efficiency cyclone is used to remove dust from the effluent gases

20 A silicon etching gas or mixture of gases may be injected through one or more nozzles for the purpose of etching wall deposits from all or part of the reactor, such gases may be elemental halides such as chlorine or bromine, hydrogen halides such as hydrogen chloride or hydrogen bromide or combinations of hydrogen and silicon tetrahalides such as silicon tetrachloride or silicon  
25 tetrabromide.

The reactor is supported upon a weigh cell, capable of weighing the reactor and contents and measuring the intermittent force exerted by the pulsing gas and the connections to and from the reactor are flexible enough to allow the slight  
30 deflection required by the weigh cell, said deflection to be less than 1mm and  
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5 preferably less than 0.5mm, and the thermal expansion of the reactor relative to the support structure, said thermal expansion to be less than 1" (25mm) and preferably less than 1/4" (6mm).

A variation on the design is where all or a portion of the non silicon containing  
10 gases are heated to a temperature below the reaction temperature outside the heating section then heated to a temperature above the reactor temperature inside the heater prior to entry to the reactor section.

In a yet further variation the second stage heater section does contain some residual silicon dust or silicon containing gases from the first stage reactor  
15 section that can form a wall deposit.

The drawings constitute a part of this specification and include exemplary embodiments to the invention, which may be embodied in various forms. It is to  
20 be understood that in some instances various aspects of the invention may be shown exaggerated or enlarged to facilitate an understanding of the invention.

25